A study of possible extra-framework cation ordering in Pbca leucite structures with stoichiometry RbCsX2+Si5O12 (X = Mg, Ni, Cd)

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A study of possible extra-framework cation ordering in *Pbca* leucite structures with stoichiometry $RbCsX^{2+}Si_5O_{12}$ (*X* = Mg, Ni, Cd).

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Introduction

Synthetic anhydrous analogues of the silicate framework minerals **leucite** ($KAlSi_2O_6$) and **pollucite** ($CsAlSi_2O_6$) can be prepared with the general formulae $A_2BSi_5O_{12}$ and $ACSi_2O_6$, where *A* is a monovalent alkali metal cation, *B* is a divalent cation and *C* is a trivalent cation. These structures all have the same topology with *B* and *C* cations partially substituting onto tetrahedrally coordinated sites (T-sites) in the silicate framework and charge balancing *A* cations sitting in extra-framework channels. The *A* cations can be replaced by ion exchange and these materials are of potential technological interest as storage media for radioactive Cs from nuclear waste [1].

We have used X-ray and neutron powder diffraction to determine and Rietveld [2] refine the *Pbca* crystal structures of leucite analogues [3-7] with the general formulae $A_2BSi_5O_{12}$, (*A* = Rb, Cs; *B* = Mg, Mn, Co, Ni, Cu, Zn, Cd). These structures all have ordered T-site cations and also have *A* cation sites fully occupied with either Rb or Cs. In this poster we report the Rietveld refinements of the *Pbca* crystal structures of three more cation ordered leucite analogues with **both Rb and Cs** on the *A* cation sites, these have the stoichiometry of $RbCsX^{2+}Si_5O_{12}$ (*X* = Mg, Ni, Cd). The *Pbca* structure has **two different sites** for *A* cations, this study is to discover whether these sites have Rb and Cs cation order?

Synthesis

$Rb_2X^{2+}Si_5O_{12}$ and $Cs_2X^{2+}Si_5O_{12}$ were prepared from appropriate stoichiometric mixtures of Rb_2CO_3, Cs_2CO_3, SiO_2, and *X*O (*X* = Mg, Ni, Cd) [3-5, 7] and then 50:50 mixtures of the Rb and Cs samples were made. For *X* = Ni the starting materials were both glasses, the mixture was sealed in a gold capsule and heated in a furnace at 1173 K for a week. For *X* = Cd and Mg the starting materials were both crystalline, the mixtures were sealed in a gold capsule (*X* = Cd) or a Pd-Ag alloy capsule (*X* = Mg) these were heated in a furnace at 1173 K for 6 hours.

Data collection and analysis

After heating the samples were removed from the metal capsules and mounted on low-background silicon wafers prior to ambient temperature X-ray powder diffraction. Data were collected for the *X* = Mg and Cd samples on a PANalytical X'Pert Pro MPD using Cu Kα X-rays and an X'Celerator area detector. For the *X* = Ni sample data were collected on a PANalytical Empyrean diffractometer using Co Kα X-rays with a PIXCEL-3D area detector. Analyses of the powder diffraction data showed that all samples were single-phase and isostructural with the *Pbca* structure of $Cs_2CdSi_5O_{12}$ [3]. Rietveld refinements were done using FULLPROF [8], using the structures of $Rb_2XSi_5O_{12}$ [4, 5 and 7] as starting models with both *A* cation sites occupied 50:50 with Rb and Cs. Figures 1 (*X* = Mg), 2 (*X* = Ni) and 3 (*X* = Cd) show the Rietveld difference plots for these structures. Table 1 shows the comparison of the refined lattice parameters and *A* cation site occupancies for $RbCsX^{2+}Si_5O_{12}$ compared to the published values for $Rb_2XSi_5O_{12}$ and $Cs_2XSi_5O_{12}$.

(Rb,Cs)2MgSi5O12 leucite

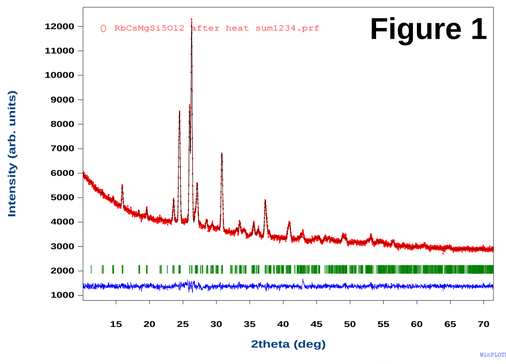

Figure 1

(Rb,Cs)2NiSi5O12 leucite

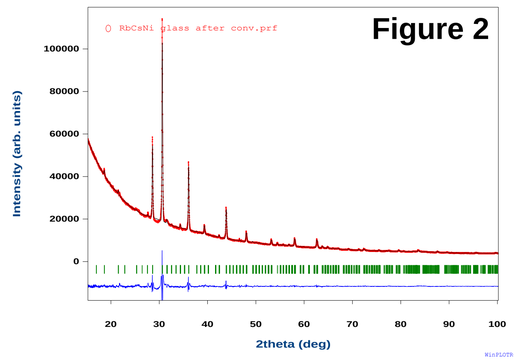

Figure 2

(Rb,Cs)2CdSi5O12 leucite

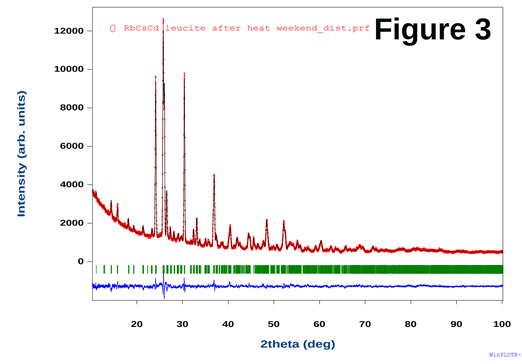

Figure 3

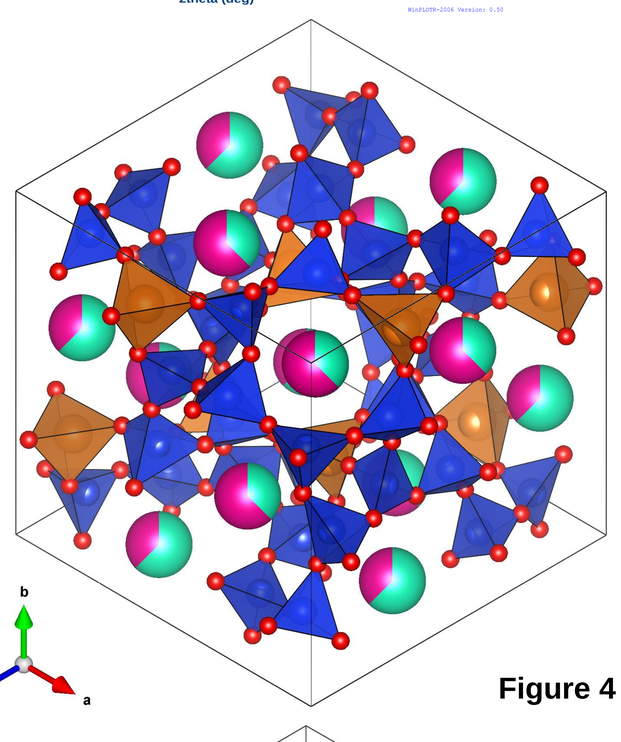

Figure 4

Figures 4 (*X* = Mg), 5 (*X* = Ni) and 6 (*X* = Cd) show VESTA [9] structure plots for $RbCsX^{2+}Si_5O_{12}$.

SiO_4 tetrahedra are shown in blue with O^{2-} anions are shown in red. MgO_4 tetrahedra are shown in orange. NiO_4 tetrahedra are shown in grey. CdO_4 tetrahedra are shown in green. Light blue (Cs^+) and pink (Rb^+) shadings show the occupancies of the two *A* cation sites.

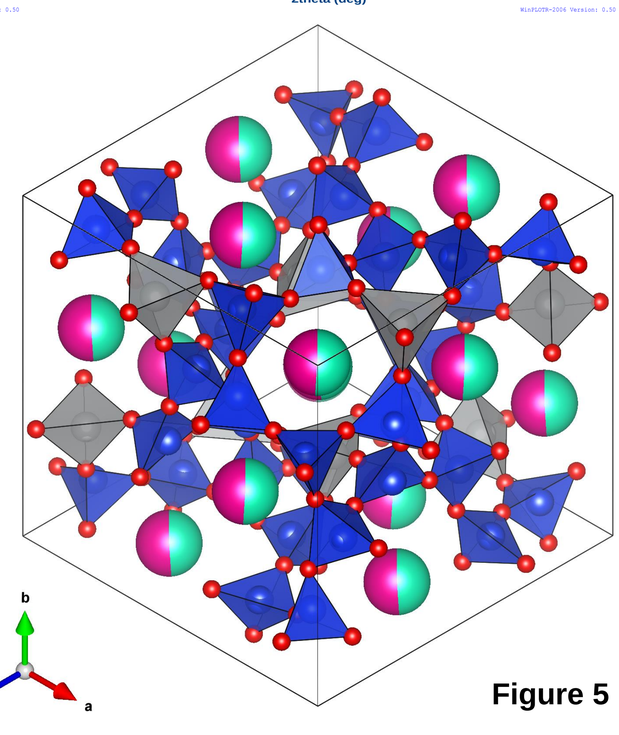

Figure 5

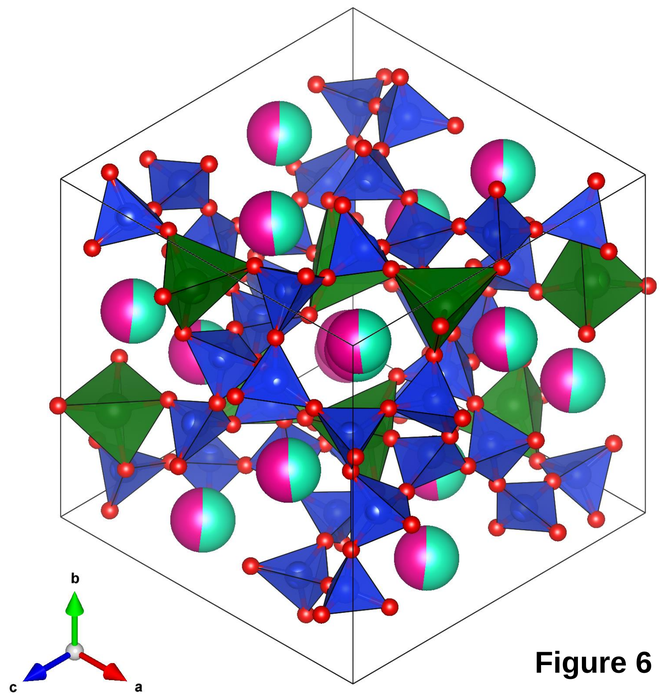

Figure 6

Discussion

Crystal structures have been refined for $RbCsX^{2+}Si_5O_{12}$ (*X* = Mg, Ni, Cd) leucite analogues from X-ray powder diffraction data. All are isostructural with their *Pbca* $Rb_2XSi_5O_{12}$ and $Cs_2XSi_5O_{12}$ analogues, with divalent *X* cations ordered onto separate T-sites than those occupied by Si.

For *X* = Mg and Ni the $RbCsX^{2+}Si_5O_{12}$ structures have unit cell volumes intermediate between that for the pure Rb and pure Cs analogues. However, for *X* = Cd the $RbCsX^{2+}Si_5O_{12}$ structures has a unit cell volume much closer to that for the pure Cs analogue.

For *X* = Mg the $RbCsX^{2+}Si_5O_{12}$ structure has partial *A* site ordering of the alkali metal Cs^+ and Rb^+ cations. However, for *X* = Ni and Cd the $RbCsX^{2+}Si_5O_{12}$ structures have complete *A* site disorder of the alkali metal Cs^+ and Rb^+ cations.

Table 1 - refined lattice parameters and *A* site occupancies

A^+ cations	Rb	Rb Cs	Cs	Rb	Rb Cs	Cs	Rb	Rb Cs	Cs
X^{2+} cations	Mg	Mg	Mg	Ni	Ni	Ni	Cd	Cd	Cd
a(Å)	13.422(1)	13.5676(9)	13.6371(5)	13.469(3)	13.5399(5)	13.6147(3)	13.4121(1)	13.6935(3)	13.6714(1)
b(Å)	13.406(1)	13.7115(1)	13.6689(1)	13.480(3)	13.563(1)	13.6568(5)	13.6816(1)	13.8031(3)	13.8240(1)
c(Å)	13.730(1)	13.5366(9)	13.7280(5)	13.442(2)	13.560(1)	13.6583(5)	13.8558(1)	13.8592(4)	13.8939(1)
V(Å^3)	2470.5(4)	2518.2(3)	2559.0(2)	2440.6(8)	2490.1(3)	2539.5(1)	2542.53(5)	2619.6(1)	2625.86(6)
A1 Rb occ.	1	0.63(3)	0	1	0.49(6)	0	1	0.52(2)	0
A1 Cs occ.	0	0.37(3)	1	0	0.51(6)	1	0	0.48(2)	1
A2 Rb occ.	1	0.37(3)	0	1	0.51(6)	0	1	0.48(2)	0
A2 Cs occ.	0	0.63(3)	1	0	0.49(6)	1	0	0.52(2)	1

Conclusions

Crystal structures have been refined for $RbCsX^{2+}Si_5O_{12}$ (*X* = Mg, Ni, Cd) leucite analogues. These are isostructural with their *Pbca* $Rb_2XSi_5O_{12}$ and $Cs_2XSi_5O_{12}$ analogues. For *X* = Mg there is partial ordering of the Rb and Cs cations over the alkali metal cation *A* sites. However, for *X* = Ni and Cd these alkali metal cations are completely disordered.

References:- [1] Gatta, G. D. *et al*. (2008). Phys. Chem. Miner. 35, 521–533. [2] Rietveld, H. M. (1969). J. Appl. Cryst. 2, 65–71. [3] Bell, A. M. T. *et al*. (1994). Acta Cryst. B50, 560–566. [4] Bell, A. M. T. & Henderson, C. M. B. (1996). Acta Cryst. C52, 2132–2139. [5] Bell, A. M. T. & Henderson, C. M. B. (2009). Acta Cryst. B65, 435–444. [6] Bell, A. M. T. *et al*. (2010). Acta Cryst. B66, 51–59. [7] Bell, A. M. T. & Henderson, C. M. B. (2016). Acta Cryst. E72, 249–252. [8] Rodríguez-Carvajal, J. (1993). Phys. B: Condens. Matter, 192, 55–69. [9] Momma, K. & Izumi, F. (2008). J. Appl. Cryst. 41, 653–658.